BIOMASS AND BIOENERGY 66 (2014) 286–300

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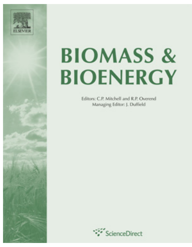

Pretreatment and fractionation of barley straw using steam explosion at low severity factor

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ARTICLE INFO

Article history:
Received 4 November 2013
Received in revised form
30 January 2014
Accepted 5 February 2014
Available online 1 March 2014

Keywords:
Biomass straw
Steam explosion
Severity factor
Chemical composition
Higher heating value
Carbon content

ABSTRACT

Agricultural residues represent an abundant, readily available, and inexpensive source of renewable lignocellulosic biomass. However, biomass has complex structural formation that binds cellulose and hemicellulose. This necessitates the initial breakdown of the lignocellulosic matrix. Steam explosion pretreatment was performed on barley straw grind to assist in the deconstruction and disaggregation of the matrix, so as to have access to the cellulose and hemicellulose. The following process and material variables were used: temperature (140–180 °C), corresponding saturated pressure (500–1100 kPa), retention time (5–10 min), and mass fraction of water 8–50%. The effect of the pretreatment was assessed through chemical composition analysis. The severity factor R_o, which combines the temperature and time of the hydrolytic process into a single reaction ordinate was determined. To further provide detailed chemical composition of the steam exploded and non-treated biomass, ultimate analysis was performed to quantify the elemental components. Data show that steam explosion resulted in the breakdown of biomass matrix with increase in acid soluble lignin. However, there was a considerable thermal degradation of cellulose and hemicellulose with increase in acid insoluble lignin content. The high degradation of the hemicellulose can be accounted for by its amorphous nature which is easily disrupted by external influences unlike the well-arranged crystalline cellulose. The carbon content of the solid steam exploded product increased at higher temperature and longer residence time, while the hydrogen and oxygen content decreased, and the higher heating value (HHV) increased.

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1. Introduction

The depleting fossil fuel resources along with global warming associated with greenhouse gas (GHG) emission has been a serious concern to the global community. Presently, this has necessitated looking for a renewable, sustainable, and environmentally friendly energy. Lignocellulosic biomass has been identified as one of the renewable, near carbon neutral,

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http://dx.doi.org/10.1016/j.biombioe.2014.02.002

and local fuel sources to complement fossil fuels and to contribute to energy security [1]. It is estimated that the worldwide annual production of lignocellulosic biomass (agricultural and forest resources) is approximately 200 Gt [1]. However, there are some challenges associated with the use of lignocellulosic biomass. Lignocellulosic biomass is a complex formation of cellulose, hemicellulose, and lignin. The lignin acts as an external crosslink binding the hemicellulose and cellulose with cellulose positioned at the inner core of the structure [2,3]. This nature of lignocellulosic biomass matrix makes it naturally resistant to the microbial and enzymatic degradation needed for biochemical conversion. Hence, the goal for the biofuel industry is to make the process technically feasible and economically attractive. Many pretreatment technologies have been applied in the past decades to deconstruct and fractionate a complex lignocellulose structure to its simpler molecules.

Canada has a large agricultural sector with barley production as the second largest crop behind wheat [4]. This implies that Canada will play a very significant role in the development of the biorefinery sector because of its contribution as a predominant supplier or source of biomass feedstock. Barley straw has a higher mass fraction of cellulose (40%) than wheat straw (30%), although wheat straw has a higher mass fraction of hemicellulose (50%) than barley straw (20%), with both substrates having similar mass fraction of lignin (15%) [5,6]. Perusal of the literature shows that a lot of research has been done on wheat straw; therefore, there is a need to explore the potential of barley straw for the biofuel industries. Hence, for these reasons as well as its higher cellulose content than wheat straw, barley straw was chosen for this work.

1.1. *Steam explosion*

Steam explosion is operated by introducing the feedstock into the reactor and heating under steam pressure (2000–5000 kPa; 200–260 °C) for a few minutes [7]. Steam explosion induces chemical effects because water itself acts as an acid at high temperatures [8]. In the course of the process, hemicellulose is hydrolyzed by acetic acid and other acids, and the hemicellulose eventually becomes water-soluble [7,8]. Cellulose is slightly depolymerized, lignin softens and is eventually depolymerized. The reaction is instantaneously interrupted by sudden opening of the reactor to depressurize the treated material which is discharged through a nozzle into a collection vessel [7]. The sudden decompression rapidly decreases the temperature and quenches the reaction at the end of the pretreatment. The rapid thermal expansion involved in the termination of the reaction opens up the particulate structure of the biomass [8]. However, at excessive conditions (high temperatures and pressures), there is degradation of xylose (a hemicellulose) to furfural and glucose (a cellulose monomer) to 5-hydroxymethyl furfural [7,9]. Furfural is an undesirable compound in a fermentation process because it inhibits microbial growth and activity [7,9]. Chornet and Overend [10] reported that the severity of thermal pretreatment depends on the combined effects of temperature and moisture particularly in the amorphous compounds in biomass. In the present study, we hypothesized that using higher biomass initial moisture content and lower temperature could damp the severe steam explosion pretreatment conditions and lead to reduction in the degradation of the xylose and glucose. Chemical consequences of thermal treatment of lignocellulosics either in a suspension (large amount of liquids present) or in steaming processes (low amount of free water present) was summarized by Chornet and Overend [10] as follows: “the extent of disaggregation of lignin-carbohydrates complexes is a function of the severity of the treatment, and the degree of depolymerization of hemicellulose and cellulose polymers and the rupture of glycosidic bonds”.

1.2. *Severity factor*

Due to the different types of available lignocellulosic biomass, a severity factor has been developed to combine and normalize the process parameters of steam explosion so as to facilitate comparisons [10]. Effort has been in progress to minimize product degradation resulting from pretreatment conditions. The rate constant of the severity factor, according to Chornet and Overend [10] can be described by the Arrhenius model:

$$k = Ae^{-\frac{Ea}{RT}} \tag{1}$$

k = rate constant; A = Arrhenius frequency factor; Ea = activation energy (kJ kg^{-1} mol^{-1}); R = universal gas constant (8.314 kJ kg^{-1} mol^{-1} K^{-1}); T = absolute temperature (K).

The reaction ordinate was developed as:

$$R_o = \int_0^t \exp\left[\frac{(T_r - T_b)}{14.75}\right] dt \tag{2}$$

R_o = reaction ordinate; t = residence time (min); T_r; = reaction temperature (°C); T_b = base temperature at 100 °C; (14.75 is the conventional energy of activation assuming that the overall process is hydrolytic and the overall conversion is first order), therefore;

$$R_o = t\exp\left[\frac{(T_r - 100)}{14.75}\right] \tag{3}$$

The log value of the reaction ordinate gives the severity factor which is used to map the effects of steam explosion pretreatment on lignocellulosic biomass.

$$\text{Severity} = \log_{10}(R_o) \tag{4}$$

Heitz et al. [11] reported that it is possible to directly translate results obtained from laboratory steam explosion pretreatment processes into industrial practice by employing the concept of a severity factor. This is similar to those used in pulping industry which integrates temperature and retention time into a single measure for the purpose of controlling the process [12].

Chum et al. [13] investigated the effect of acid catalyzed pretreatment on aspen (*Populus tremuloides*). These authors included a pH term to equation (7) above to compensate for the contribution of the added acid. Severity parameter that reflects acidity or alkalinity functions can be very useful tool in the planning of experiments for pretreatment process that requires the addition of catalyst (acid/base) [13]. However, it was concluded that the reaction ordinate concept does not appear to be universally valid [14]. Nonetheless, the reaction ordinate remains a useful bookkeeping method of reporting steam explosion conditions.

1.3. *Heating value of biomass*

The heating value of biomass is an important parameter for the planning and control of power plants. The heating (calorific) value of lignocellulosic biomass feedstocks is a representative of the energy content they possess as potential biofuel. The gross calorific value (higher heating value, HHV) and the net calorific value (lower heating value, LHV) at constant pressure condition measure the enthalpy change of combustion with and without water condensation, respectively [15–17]. The heating values of biomass materials can be determined experimentally using an adiabatic bomb calorimeter or they can be estimated by using mathematical models based on the chemical composition, proximate or ultimate analysis of the biomass fuel [18,19]. The theoretical HHV of barley straw has been reported as 17.31(MJ kg^{-1}, dry basis) by Annamalai et al. [17].

Previous studies done on the optimization of steam explosion of lignocellulosic biomass focused on the effects of steam explosion temperature, retention time, biomass screen size, and pH. However, little or no work has been done on effects of feedstock initial moisture content on the severity of the steam explosion technologies. Consequently, the objective of this current investigation was to study steam explosion pretreatment of barley straw as the biomass substrate is affected by the initial moisture content of the biomass, temperature (or pressure) of steam, and retention time of the treated biomass in the steam reactor.

2. Materials and methods

2.1. *Sample collection and preparation*

Barley straw of the ‘Xena’ variety was obtained in October, 2009 from RAW Ag Ventures Limited (Maymont, SK, Canada), and was grown at 52.667297° N and 107.794311° W. The straw was ground using a hammer mill (Serial no. GM13688; Glen Mills Inc., Maywood, NJ, USA) with screen size of 1.6 mm to increase the surface area of the biomass. A dust collector (House of Tools, Model no. DC-202B, Saskatoon, SK, Canada) was connected to the outlet of the hammer mill to provide flow of the biomass in and out of the hammer mill and to control dust during operation. The initial mass fraction of water in the straw was 8.09%. The moisture content was measured based on ASABE standard method, ASAE S358.2 (2008). This test was performed in replicates of three. For details of the measurement, calculations, and results of the physical characteristics of the barley straw grind, see Iroba et al. [20].

The samples were re-conditioned to the desired moisture content by spraying a pre-calculated amount of water on the samples to targeted moisture of the biomass, mixed manually and kept in a conditioned environment (~6 °C) for 48 h before the pretreatment process.

Three process parameters were investigated for the optimization of steam explosion process. These variables (temperature (with corresponding saturated pressure), moisture content, and retention time) were investigated to determine the optimum condition for steam explosion pretreatment of biomass barley straw grind with minimal formation of inhibitors, and also to enhance formation of biomass pellets with good physical quality characteristics which was discussed in Iroba et al. [21]. The experimental design was based on a completely randomized approach, which resulted in 18 treatment combinations. Table 1 lists the levels of the independent variables:

A temperature range of 140–180 °C was selected so as to pretreat the biomass within the softening temperature of lignin and avoid or limit the thermal degradation of cellulose and hemicellulose and lignin. Fengel and Wegener [22] reported that the softening temperature of lignin is in the range of 130–190 °C. The thermal stability of probable linkages between lignin and polysaccharides was compromised at temperatures above 200 °C [22]. Thermal degradation of lignin starts at 270–280 °C [22].

2.2. *Steam explosion process description and operation procedures*

The steam explosion pretreatment set up used for this investigation is located at the Clean Energy Research Center, University of British of Columbia, Vancouver, BC, Canada. Fig. 1 below shows the process flow sheet of the closed system steam explosion batch unit:

The unit consists of a 2 L steam generator, which generates saturated steam, and a 1 L reactor for steaming lignocellulosic biomass feedstocks. A 3 zone tubular furnace (Lindberg/Blue M, STF55666C, Thermo Fisher Scientific Inc., Waltham, MA, USA) installed inside the boiler chamber was used for the generation of the steam heat. The 1 L reactor was equipped with a 12.7 mm diameter ball valve (B-1), controlled by an electrical actuator for sudden discharge of the treated biomass into the collection vessel at ambient pressure. The service and maintenance heat of the reactor and the steam-line were regulated by a temperature controller (T1 and T4). The details and functions of valves in the experimental set-up unit are summarized elsewhere [23]. Temperatures and pressures were measured by 1.6 mm diameter K-type thermocouples, T1–T4 (Omega, Stamford, CT, USA) and digital pressure transducers, P1–P2 (Omega, Stamford, CT, USA), respectively. Data were collected by LabView 8.2 software (National Instruments, Austin, TX, USA).

2.2.1. *Steam generation*

To generate the saturated steam required for the explosion in each experiment, about 350 cm^3 of distilled water was

Table 1 – Independent variables with corresponding levels.

Variables	Levels
Temperature (°C)	140, 160, 180
Moisture content (% mass fraction)	8, 30, 50
Retention time (min.)	5, 10

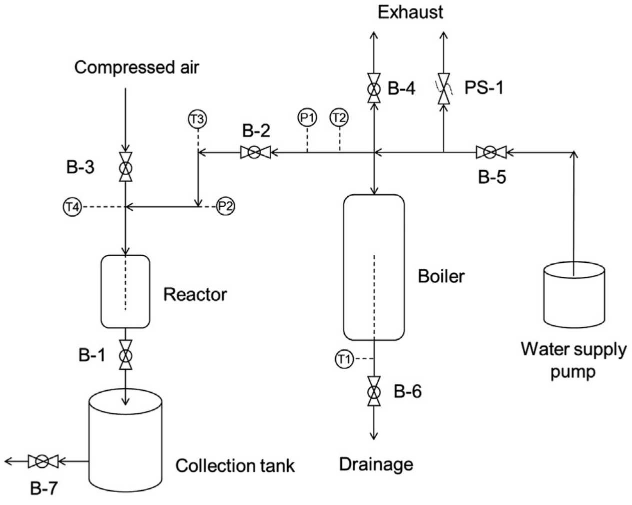

Fig. 1 – Process flow sheet of the closed system steam explosion unit (B: Ball valve, PS: Pressure relief valve, P: Digital pressure transducer, T: Thermocouple) [23].

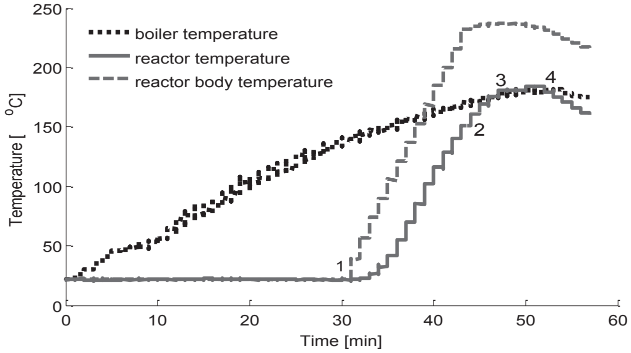

Fig. 2 – Typical temperature profile of an experiment (180 °C, 50% moisture content (w.b.), and 5 min retention time); Point 1 = reactor temperature controller was turned on; Point 2 = ball valve B-2 was opened; Points 3–4 = preset retention time; point 4 = ball valve B-1 was suddenly opened.

pumped from a water tank into the steam generator using a water pump. Prior to pumping the water, ball valves B-4 and B-6 were opened to purge the left over water in the steam boiler from the previous experiment. Any trapped air within the system was vented out by opening of B-4 valve which facilitated faster water drainage. These valves were closed after the water discharge. Ball valve B-5 was opened during the water pumping and closed thereafter. The actual water used for the steam generation was calculated from the difference between the loaded and the discharged water. Approximately 50 cm^3 of water was used as steam for each run of experiment. Ball valve (B-2) always remained closed during the purging and pumping process. Prior to addition of the barley straw grind into the reactor, ball valve (B-1) was closed so as to contain the loaded biomass within the reactor. Biomass of about 30–28 g was loaded through the small opening (about 10 mm) at the top of the reactor. Thereafter, ball valve B-3 (closed) was connected to the opening. Ball valve B-3 was also connected to compressed gas on the other end so as to facilitate the discharge of the treated sample.

2.2.2. *Steam explosion experimental runs*

After adding biomass into the reactor (at room temperature and initial reactor pressure of about 0–14 kPa) and pumping water into the steam generator, the temperature regulator of the steam boiler was turned on and set to a preset temperature (140–180 °C, depending on the treatment combination). It took between 30 and 50 min to reach the preset temperature depending on the treatment combinations. When the temperature reached regulated temperature (40 °C away from the preset temperature), the reactor temperature controller was turned on (Point 1 in Figs. 2 and 3) and set to the same preset temperature as the steam boiler. This maintained thermal equilibrium and avoided heat loss from the steam to the reactor as well as preventing condensation within the reactor. The target was for the reactor temperature and the generated steam temperature to get to the preset temperature (140–180 °C depending on the treatment combinations) simultaneously. When the temperature of the boiler reached the preset temperature with a corresponding saturated pressure, ball valve B-2 was opened (point 2 in Figs. 2 and 3; for about 2–3 min depending on the treatment combinations) to transport the generated steam from the boiler to the reactor to treat the biomass for a pre-specified time. The generated steam was supplied to the reactor through the small opening (about 10 mm) at the top of the reactor. This led to a decrease in the boiler pressure and an increase in the reactor pressure as shown in Fig. 3. This valve was closed when the same pressure (ranges from 500 to 1100 kPa depending on the treatment combinations) was observed in the boiler and the reactor. After the elapsed retention time (Points 3–4 in Figs. 2 and 3), ball valve B-1 was opened (point 4 in Figs. 2 and 3) to suddenly decompress the system, and the treated sample was discharged into a bag in the collection tank at ambient conditions (101 kPa, 23 °C). The collected steam exploded solid biomass product was weighed to determine the mass loss or

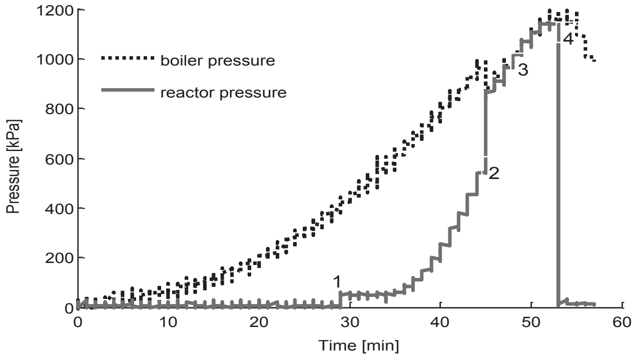

Fig. 3 – Typical pressure profile of an experiment (180 °C, 50% moisture content (w.b.) and 5 min retention time); Point 1 = reactor temperature controller was turned on; Point 2 = ball valve B-2 was opened; Points 3–4 = preset retention time; point 4 = ball valve B-1 was suddenly opened.

gain and kept in sealed Ziploc containers at 6 °C for further analysis. Each test was replicated twice.

2.2.3. *Data acquisition and control*

Data acquisition and logging in this experiment were done using LabView 8.2 software (National Instruments, Austin, TX, USA). The data logging was one data point per second. The ball valve (B-1) used for the sudden decompression and opening of the bottom outlet of the reactor (to discharge the steam treated biomass) was controlled by Labview software.

Due to the small inlet opening (about 10 mm) as well as the moist nature of the samples, loading the samples into the reactor was very difficult. As such, a thin rod was used to push down the samples as they were loaded into the reactor. This resulted in the loaded samples sticking to the walls of the reactor. Since the heat source of the reactor was wrapped round it, the heat transfer was by conduction which comes from outside to inside of the reactor. This resulted in the wall of the reactor having a higher temperature than the inside of the reactor.

2.3. *Chemical composition analysis*

The chemical composition analysis was performed using the National Renewable Energy Laboratory standard (NREL) [24]. The NREL standard uses a two-step acid hydrolysis to fractionate the biomass into forms that are more easily quantified. The first step uses 72% H_2SO_4, while the second step uses 4% H_2SO_4.

Chemical composition analysis was done on the structural carbohydrates and lignin of the steam exploded and non-treated biomass. The lignin fractionates into acid insoluble and acid soluble material. The acid insoluble lignin (AIL) is the residue (remaining solids) from the hydrolysis suspension. The acid soluble lignin (ASL) was measured using two different NREL standard approaches; the first was using UV–Vis spectroscopy (Helios Aquamate v7.09 spectrophotometer, Thermo-Scientific, Cambridge, England). The second approach for measuring the ASL was done using the Ultra Performance Liquid Chromatography (UPLC) (Acquity 2004–2010, Waters Corp., Milford, MA, USA) which has the capability of separating and quantifying the various lignin components.

During the two-step acid hydrolysis, the polymeric carbohydrates (cellulose and hemicellulose) were hydrolyzed into monomeric forms (xylose, arabinose, mannose, glucose, and galactose), which are soluble in the hydrolysis liquid. These were measured by UPLC. The furfurals: 1) 5-hydroxylmethyl furfural; and 2) furfural, and the lignin moieties (components): 1) H acid lignin group (4-hydroxybenzoinc acid); 2) G acid lignin group (vanillic acid); 3) S acid lignin group (syringic acid); 4) H aldehyde lignin group (4-hydroxybenzaldehyde); 5) G aldehyde lignin group (vanillin); and 6) S aldehyde lignin group (syringaldehyde) were also measured using the UPLC. The spectra generated from the UPLC were integrated and extracted using Empower 2 software (Waters Corp., Milford, MA, USA). The extracted integrated peak area was correlated to the concentration of the standards using a pre-determined regression equation from dilution series using Microsoft Excel. Each test was replicated twice. For details on the chemical compositions analysis and regression see Iroba et al. [20].

2.4. *Determination of ash in biomass*

The ash content, which is a measure of the mineral content and other inorganic matter (structural or extractable) in the biomass, was measured as part of the total composition. Structural ash, which is inorganic material, is bound in the physical structure of the biomass, while the extractable ash is the inorganic material that can be removed by washing or extracting the material [25]. The ash content of the biomass samples was determined based on National Renewable Energy Laboratory standard (NREL) [25]. About 0.5–2.0 g of the oven dried samples (dried @ 105 °C overnight) was weighed into a tared, dried crucible. The weighed crucible and the sample were placed in a muffle furnace (Model 650-14, Fisher Scientific, Pittsburgh, PA, USA) equipped with a thermostat with ramping program. Samples were heated to 105 °C, held at 105 °C for 12 min, ramped to 250 °C at 10 °C min^{-1}, held at 250 °C for 30 min, ramped to 575 °C at 20 °C min^{-1}, and held at 575 °C for 180 min. Then the temperature was decreased to 105 °C and held at 105 °C until the samples were removed. Each test was replicated twice and the ash content was computed as the percentage of residue remaining after the dry oxidation at 575 °C.

2.5. *Ultimate analysis of steam exploded and non-treated lignocellulosic biomass*

In order to ascertain whether carbonization occurred during steam explosion process, the elemental composition analysis of the steam exploded and non-treated barley straw was performed. The measurement was done using the CHNS elemental analyzer Vario EL III (Elementar Analysensteme GmbH, Serial No.: 11014041, Hanau, Germany). This set up is a fully automatic instrument for a speedy and quantitative determination of CHNS (Carbon, Hydrogen, Nitrogen, and Sulfur, respectively). Sulfanic acid (Sulfonilic acid) was used as standard for the system calibration. About 4.05–5.90 mg of the homogenized steam exploded and non-treated barley straw grind (0.354 mm screen size) carefully packed in tin foil (smooth wall tin capsules, Isomass Scientific Inc., elemental microanalysis, BN 182103) was combusted explosively in a highly oxygenated environment to produce the elements C, H, N, and S, in addition to the molecular nitrogen (N_2) and the oxidation products: O_2, H_2O, NO_x, SO_2, and SO_3. Each test was replicated twice.

2.6. *Higher heating values*

The HHV was experimentally measured using the oxygen bomb calorimeter (Parr Instrument Company, Model 1281, Moline, IL, USA). The procedure involves burning about 500–700 mg of pelleted sample in an oxygen-filled metal bomb submerged in a measured quantity of water, all held within a thermally insulated chamber. The exact rise in water-temperature resulting from combustion of sample was used to calculate the amount of heat units liberated, also referred to as gross energy or combustible energy, using equations (5) and

(6) (Parr Instrument Company manual, Model 1281, Moline, IL, USA):

$$W = \frac{Hxm + E_1 + E_2}{T_f - T_a} \quad (5)$$

W = Energy equivalent of calorimeter in MJ °C^{-1}; H = Heat of combustion of standard benzoic acid in MJ kg^{-1}; m = Mass of benzoic acid in kg; T_a = Temperature at the time of firing (°C).

T_f = Final maximum temperature (°C); E_1 = Correction for acid formation; E_2 = Correction for heat of combustion of fuse wire

$$H_g = \frac{[Wx(T_f - T_a)] - (E_1 + E_2)}{\text{weight of sample}} \quad (6)$$

where H_g = Gross heat of combustion of the sample in MJ kg^{-1}.

The mass yield and energy recovery were evaluated using the equations below according to Yan et al. [26] and Ferro et al. [27]:

$$MY = \left(\frac{M_{SE}}{M_{NT}}\right) \times 100\% \quad (7)$$

$$ER = \frac{CV_{SE} \times MY}{CV_{NT}} \quad (8)$$

where MY = mass yield, M_{SE} = mass of dried steam exploded solid, M_{NT} = Mass of dried non-treated solid, and ER = energy recovery, CV_{SE} is the calorific value of the steam exploded biomass product and CV_{NT} is the calorific value of the non-treated material.

2.7. *Degree of carbonization (DOC)*

The DOC was evaluated as:

$$DOC = \frac{CV_{SE}}{CV_{NT}} \quad (9)$$

where CV_{SE} is the calorific value of the steam exploded biomass product and CV_{NT} is the calorific value of the non-treated material.

2.8. *Color measurement*

The color difference between the pretreated and non-treated was measured and compared using the HunterLab Color Analyzer (Hunter Associates Laboratory Inc, Reston, VA, USA). The color was characterized using a three-dimensional color parameters (CIE L^*, a^* and b^*). The scale L^* ranges from 0 for black to +100 for white. The a^* and b^* have no specific numerical limits; positive a^* is red; negative a^* is green; positive b^* is yellow; negative b^* is blue. The total color difference (ΔE^*) was also computed using equation (10) [28]. This single value takes into account the differences between the L^*, a^*, and b^* of the pretreated and the control (non-treated) material. Three replicates was performed for each sample.

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (10)$$

$\Delta L^* = L^*_{Treated} - L^*_{NT}$; $\Delta a^* = a^*_{Treated} - a^*_{NT}$; $\Delta b^* = b_{*Treated} - b^*_{NT}$. These parameters ΔL^*, Δa^*, and Δb^* indicate how much the non-treated (NT) and the pretreated differ from one another in L^*, a^*, and b^*.

2.9. *Statistical analysis*

Experimental data were statistically analyzed via analysis of variance (ANOVA) using simple linear regression model. The ANOVA was conducted at 5% significance level using IBM SPSS Statistics (Superior Performing Statistical Software, version 20 for Windows, 2012; IBM, Armonk, NY, USA).

3. Results and discussion

Figs. 2 and 3 show the typical temperature and pressure profiles, respectively of an experiment at 180 °C, 50% mass fraction of water, and 5 min retention time. The profiles depict good agreement between the reactor and steam boiler temperatures and pressures. Fig. 2 shows that the heat source to the reactor caused a temperature difference between the outside (reactor body) and inside portion of the reactor. Point 1 in Figs. 2 and 3 represents the time the reactor temperature controller was turned on, Point 2 shows the time ball valve B-2 was opened to transfer the generated steam from the boiler to the reactor. This led to a decrease in the boiler pressure and an increase in reactor pressure. Points 3-4 depict the preset retention time (5 min for this treatment combination), while point 4 is the time at which ball valve B-1 (at the outlet bottom of the reactor) was opened to suddenly decompress the system.

Fig. 4 shows the steam exploded and non-treated biomass obtained from three different studies. This reflects that different biomass products can be obtained from steam explosion pretreatment depending on the nature and design of the steam explosion set up and the intended end use of the treated biomass products.

3.1. *Severity factor*

The severity factor used in this study combined temperatures (140–180 °C) and time (5–10 min) of the hydrolytic process in a single ordinate (R_o). Table 2 shows the severity of the pretreatment condition.

The severity factor obtained ranged from 1.88 to 3.36 depending on the temperature and residence time. It shows that the severity factor increased with temperature and time. Increasing temperature and time of steam explosion pretreatment will subsequently result in higher stringent pretreatment conditions of biomass. In the formulation of severity factor model, moisture content of biomass was not incorporated. The current investigation used moisture content of biomass to create a buffer effect and as a tool to dampen the severity of the pretreatment condition, and subsequently moderate the formation of inhibitors such as furfural. Therefore, the changes observed in the data suggested that the treatment severity (reaction ordinate) should also incorporate an additional function (moisture or acid or alkaline function) which will directly affect the hydrolytic mechanisms. This investigation shows that the reaction ordinate plays a vital role in the thermal degradation of cellulose and hemicellulose, in breaking the lignified matrix, changes in the ash content and color, elemental compositions, and inhibitor formation, as well as changes in the higher

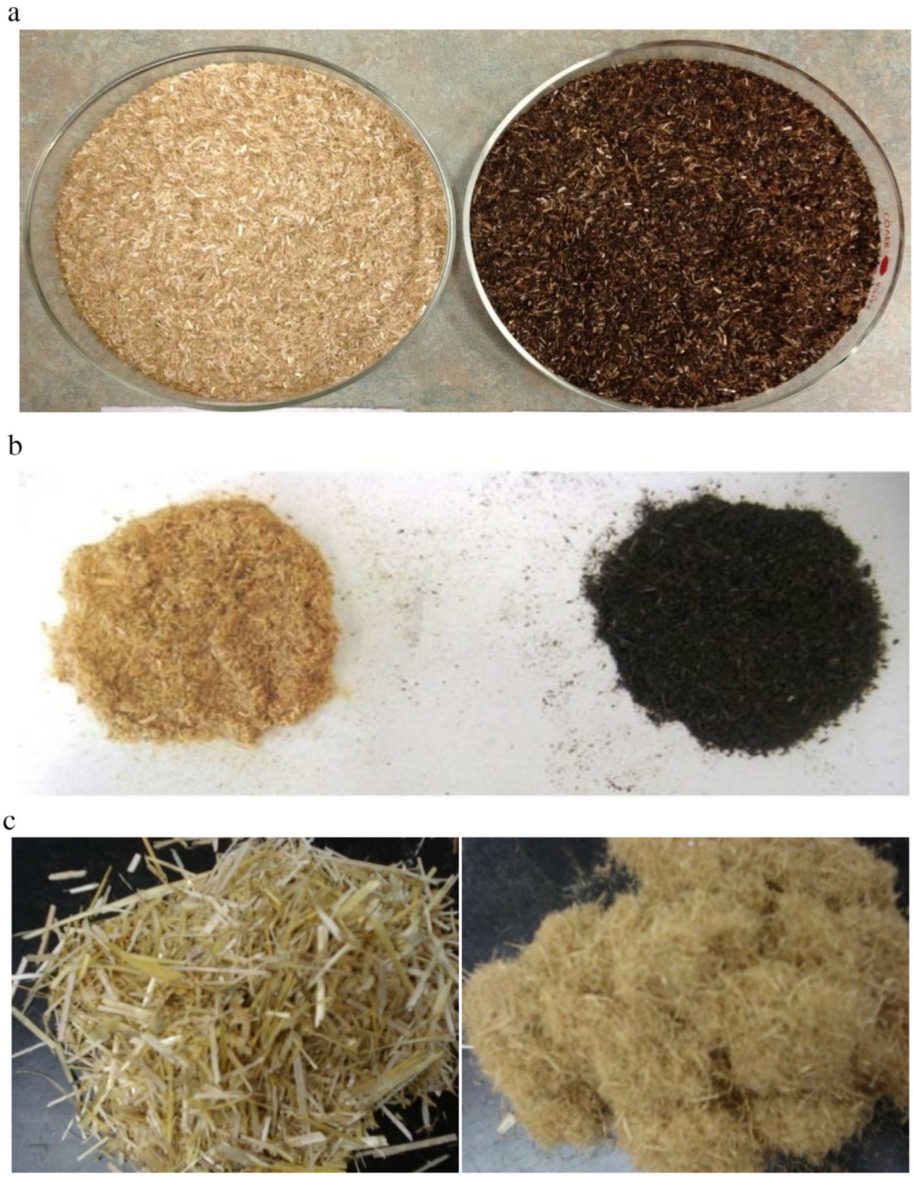

Fig. 4 – a. Comparison of non-treated and steam exploded barley straw grind at 180 °C and 5 min retention time, with initial moisture content of 50% (w.b.) and ground using a hammer mill with 1.6 mm screen size (this present study). b. Comparison of non-treated and steam exploded (right) spruce grind at 220 °C and 5 min retention time, with initial moisture content of 10% (w.b.) and ground using a hammer mill with 1.6 mm screen size, adapted from Tooyserkani et al. [29]. c. Comparison of non-treated and steam exploded (right) barley straw grind at 180 °C and 4 min, with initial moisture content of 13.5% (w.b.) and ground using a hammer mill with 30 mm screen size, adapted from Adapa [30].

Table 2 – Severity factor of the steam explosion process calculated based on equations (3) and (4).

Reaction temperature (°C)	Residence time (min)	Severity factor
140	5	1.88
160	5	2.47
180	5	3.05
140	10	2.18
160	10	2.77
180	10	3.36

Number of replicates, $n = 2$.

heating value of the pretreated biomass. Angles et al. [31] applied the severity factor to the steam explosion of softwood with combined temperatures ranging from 176 to 231 °C and time (2.5–5.5 min) of the hydrolytic process in a single ordinate (R_o). These authors reported that the severity factor range was modified from $\log R_o = 2.6$ to $\log R_o = 4.6$. Chornet and Overend [10] reported a severity factor of 2.6–4.2 during steam explosion treatment of *Populus deltoides*. It was observed that the yield of sugars and degree of polymerization decreased with increasing severity factor.

Toussaint et al. [7] and Heitz et al. [11] demonstrated that the higher the operating conditions (temperature and time), the higher was the severity factor (R_o), resulting in a higher recovery of cellulose and lignin, which enhanced the accessibility and digestibility of cellulose. However, they stated that this recovery is at the expense of increasing the destruction and degradation of hemicellulose. It was suggested that the optimum treatment severity of each of the polymer fractions would probably involve a two-stage treatment cycle, with the removal of the bulk of the hemicellulose and lignin at low severity and a post-treatment to obtain the cellulose in high purity though at a low degree of polymerization [11].

3.2. *Chemical composition of steam exploded and non-treated lignocellulosic biomass*

3.2.1. *Steam treatment on lignin*

Table 3 shows that as the temperature increased, the AIL increased. This may be due to the carbonization of the sample resulting from the direct contact of biomass with the walls of the reactor. The analysis of variance performed on the data shows that temperature had a significant effect ($P < 0.01$) on the AIL. At a higher temperature (180 °C), exothermic reaction takes place, resulting in the degradation of hemicellulose and cellulose. Hemicellulose degrades easily and some volatile organic compounds vaporize as volatile components, while cellulose behaves as a fixed carbon (solid combustible residue). This may account for the increase in the acid insoluble lignin content. The percentage AIL increase was between 1.61 and 91.28% as compared to the non-treated biomass. This may also be attributed to lignin's high resistance to thermal degradation during the steam explosion process. Lam et al. [32] investigated the steam explosion of Douglas Fir (*Pseudotsuga menziesii*) at a reaction temperature of 200–220 °C and a retention time of 5–10 min. These researchers reported that there was increase in total insoluble lignin content from 30 to 43% contributed by the thermal degradation of hemicellulose during the steam explosion treatment. Chen and Kuo [33] reported that cellulose and lignin are both locked in biomass from the mild carbonization process. This indicates that the degraded cellulose may appear as residue resulting to the increase in the AIL. At the investigated temperatures in this current study the steam exploded biomass gave off moisture, began to turn brown, lost its hygroscopic properties and became more friable than non-treated biomass. Similar results have been reported by Excoffier et al. [34] and Ferro et al. [27] on lignocellulosic biomass. This current study shows that AIL increased as the moisture content decreased from 50 to 8% (mass fraction of water) Statistical analysis showed that moisture content of biomass had a significant effect ($P < 0.01$) on the AIL. This demonstrates that biomass initial moisture content has buffer effect by damping the severity of the pretreatment condition; thereby, avoiding the degradation of the amorphous portion of the structural carbohydrates that could be deposited as residue and subsequently increasing the quantity of AIL in the treated biomass. The interaction between temperature and moisture content and also between moisture content and retention time had a statistically significant effect ($P < 0.01$) on the AIL. The interaction among the three variables (temperature, moisture content, and retention time) also had a significant effect on the AIL. It can be observed from Table 3 that the higher are the temperature and retention time, the higher is the total acid soluble lignin moieties content. At higher temperature and retention times the biomass matrix was deconstructed, which enhanced the quantitation of the total acid soluble lignin moieties. Cullis et al. [35] reported that as the relative severity increased, the extent of lignin modification also increased. This current investigation also depicts that the total acid soluble lignin increased up to a maximum of about 33% as compared to the non-treated biomass. The higher is the moisture content, the lower is the total acid soluble lignin moieties, because of the buffer effect of moisture and it requires higher energy to evaporate the moisture before deconstructing the biomass matrix. Cullis et al. [35] studied the effect of initial moisture

Table 3 – Soluble and insoluble lignin of steam exploded and non-treated barley straw.

Temperature (°C)	Moisture content (% mass fraction)	Retention time (min)	AIL (%)	ASL (%) using UV–Vis Spec. (%)	Total acid soluble lignin (ng/mg)
NT	8	–	21.22 (0.36)	1.38 (0.03)	265.94 (8.87)
140	8	5	23.79 (1.44)	1.35 (0.11)	307.20 (4.88)
160	8	5	22.72 (0.43)	1.38 (0.02)	311.50 (10.26)
180	8	5	40.58 (2.44)	0.81 (0.04)	322.10 (11.35)
140	30	5	22.05 (0.17)	1.53 (0.04)	249.18 (20.52)
160	30	5	21.69 (0.80)	1.36 (0.06)	244.74 (6.19)
180	30	5	33.01 (1.20)	1.21 (0.06)	301.54 (12.20)
140	50	5	21.18 (0.10)	1.45 (0.01)	223.26 (11.39)
160	50	5	23.31 (0.08)	1.29 (0.10)	230.84 (32.51)
180	50	5	25.04 (0.66)	1.30 (0.04)	249.35 (15.83)
140	8	10	21.56 (0.61)	1.43 (0.08)	304.68 (1.73)
160	8	10	21.66 (0.55)	1.39 (0.05)	303.53 (6.22)
180	8	10	32.75 (0.36)	1.09 (0.07)	352.27 (11.10)
140	30	10	21.25 (0.45)	1.47 (0.04)	302.35 (4.65)
160	30	10	20.90 (0.20)	1.39 (0.04)	306.34 (15.71)
180	30	10	37.31 (1.88)	0.85 (0.04)	282.45 (27.76)
140	50	10	21.00 (0.26)	1.42 (0.05)	303.10 (10.08)
180	50	10	31.82 (0.40)	1.04 (0.05)	341.92 (5.40)

Value in parentheses = standard error; number of replicates, $n = 2$; NT = non-treated biomass; AIL = acid insoluble lignin; ASL = acid soluble lignin; Vis Spec. = visible spectroscopy; all % values are in mass fraction.

content and chip size on the bioconversion efficiency of softwood lignocellulosics. It was reported that moisture content plays an influential role in the severity of pretreatment, as it greatly influences the ability of heat and chemicals to penetrate wood. In this present investigation, analysis of variance performed on the data shows that temperature, retention time, and moisture content had a significant effect ($P < 0.05$, $P < 0.01$, and $P < 0.01$, respectively) on the total soluble lignin moieties. The interaction between moisture content and retention time, and the interaction among moisture content, retention time, and temperature had a significant effect ($P < 0.05$) on the soluble lignin moieties.

3.2.2. *Steam treatment on inorganics and furfurals*

The ash content in the steam explosion pretreated ground barley straw increased as the temperature and retention time increased (Table 4). Both variables had a significant effect ($P < 0.01$) on the ash content of the steam exploded biomass. This could also be due to the degradation of the amorphous portion of the hemicellulose and cellulose. High ash content is not a desirable quality of biomass feedstock for thermochemical conversion; however, the percentage increase (5.68–28.10%) in ash content of steam explosion pretreated barley grind is not so high as to drastically affect biomass combustion. In comparison with the non-treated biomass, it is evident that the three independent variables studied have a strong contribution to the dependent variables (ash content and AIL).

The formation of furfural was also dependent on the severity of the pretreatment conditions. The higher are the temperature and retention time, the higher is the furfural content (Table 4). This is due to the reactions and degradations of xylose and glucose from hemicellulose and cellulose, respectively that takes place at severe conditions. Moisture content varied inversely with furfural content. The higher the moisture content, the lower is the furfural content, because the system was dampened and subsequently reduced the harsh pretreatment environment that would have led to formation of high degree of inhibitors. Analysis of variance showed that moisture content significantly affected ($P < 0.05$) the formation of furfural. Toussaint et al. [7], Tanahashi et al. [9], Chornet and Overend [10], and Kaar et al. [14] reported that at excessive conditions (high temperatures and pressures) during steam explosion, degradation of xylose to furfural and glucose to 5-hydroxymethyl furfural occurred. Furfural is an undesirable compound in fermentation because it inhibits microbial growth and activity [10]. Chornet and Overend [10] and Wang et al. [36] reported that the retention time and temperature are the process parameters required for the optimization of steam explosion process. However, these researchers demonstrated that long retention time increases the production of inhibitory substances, and has to be minimized to avoid this.

3.2.3. *Steam treatment on cellulose and hemicellulose*

Temperature played an important role in steam explosion process (Table 5). In comparison with the non-treated biomass, it is evident that temperature, moisture content, and retention time had a significant effect on the cellulose and hemicellulose content. The degradation of simple sugars increased at higher temperature and retention time. Also, higher moisture content resulted in less degradation of the simple sugars. High feedstock moisture content acts as acid catalyst to hydrolyze biomass during steam explosion. However, the direct contact of biomass with the walls of the reactor will limit and affect the extent of the hydrolysis. Therefore, a combination of carbonization and acid catalyzed hydrolysis occurred which ultimately led to the degradation of the simple sugars and increase in the AIL. These results indicated that the hemicellulose contained in the biomass was highly degraded compared to cellulose. Cellulose loss (degradation) was between 58 and 77%, while hemicellulose degradation was between 79 and 89%. The high degradation of hemicellulose was due to its amorphous nature, which

Table 4 – Furfurals and ash content of steam exploded and non-treated barley straw.

Temperature (°C)	Moisture content (% mass fraction)	Retention time (min)	Average furfural (%)	Ash content (%)	Increase/decrease in ash (%)
NT	8	–	4.04 (0.11)	5.42 (0.06)	0.00
140	8	5	5.17 (2.97)	5.75 (0.09)	5.95
160	8	5	5.70 (2.17)	5.74 (0.05)	5.86
180	8	5	6.29 (0.33)	6.93 (0.16)	27.82
140	30	5	3.99 (0.20)	5.86 (0.01)	8.09
160	30	5	5.13 (0.35)	5.40 (0.01)	−0.34
180	30	5	5.86 (0.14)	6.39 (0.17)	17.90
140	50	5	4.51 (2.74)	5.75 (0.26)	6.05
160	50	5	3.82 (1.40)	5.82 (0.08)	7.24
180	50	5	5.70 (0.19)	6.16 (0.15)	13.61
140	8	10	5.99 (2.87)	5.92 (0.00)	9.21
160	8	10	5.98 (0.44)	6.01 (0.26)	10.77
180	8	10	7.95 (0.24)	6.79 (0.21)	25.22
140	30	10	4.98 (0.55)	5.73 (0.14)	5.68
160	30	10	4.70 (1.13)	6.22 (0.48)	14.76
180	30	10	5.74 (0.54)	6.95 (0.06)	28.10
140	50	10	4.15 (2.48)	5.80 (0.15)	6.99
180	50	10	5.87 (0.28)	6.81 (0.34)	25.48

Value in parentheses = standard error; number of replicates, $n = 2$; NT = non-treated biomass; all % values are in mass fraction.

Table 5 – Cellulose and hemicellulose content of steam exploded and non-treated barley straw.

Temperature (°C)	Moisture content (% mass fraction)	Retention time (min)	Cellulose (%)	Cellulose loss (%)	Hemicellulose (%)	Hemicellulose loss (%)
NT	8	–	38.83(9.10)	–	31.68(8.86)	–
140	8	5	11.19(0.36)	71.20	3.42(0.05)	89.21
160	8	5	11.17(1.14)	71.23	3.29(0.06)	89.61
180	8	5	9.58(0.01)	75.32	3.74(0.63)	88.19
140	30	5	14.82(0.17)	61.83	3.80(0.07)	88.01
160	30	5	14.63(1.36)	62.34	4.13(0.05)	87.75
180	30	5	12.07(0.40)	68.91	3.88(0.48	81.11
140	50	5	15.81(0.90)	59.28	6.58(0.36)	79.22
160	50	5	14.51(1.07)	62.63	5.11(0.82)	83.88
180	50	5	15.77(0.16)	59.38	5.23(0.55)	83.49
140	8	10	10.02(0.34)	74.20	3.90(0.35)	87.69
160	8	10	9.11(0.47)	76.53	4.47(1.38)	85.89
180	8	10	8.74(1.15)	77.49	3.23(0.06)	89.81
140	30	10	15.38(1.11)	60.39	5.03(0.56)	84.12
160	30	10	13.57(0.43)	65.07	6.59(0.13)	79.20
180	30	10	12.70(1.29)	67.31	4.54(0.05)	85.67
140	50	10	16.02(0.06)	58.76	6.33(0.67)	80.02
180	50	10	12.35(2.13)	68.21	4.69(0.58)	85.20

Value in parentheses = standard error; number of replicates, $n = 2$; NT = non-treated biomass; all % values are in mass fraction.

degrades easily and evaporates as volatile components during the carbonization process. Presumably, the crystallinity of cellulose was responsible for the less degradation. These degradations can be explained by considering the monomers of hemicellulose and cellulose which consist primarily of sugars. Statistical analysis shows that temperature and moisture content had a significant effect ($P < 0.01$) on the structural and chemical compositional changes of cellulose. Temperature also significantly affected ($P < 0.01$) the changes associated with hemicellulose. Degradation of cellulose and hemicellulose during steam explosion/thermal pretreatment of biomass has been reported by Toussaint et al. [7], Excoffier et al. [34], Ferro et al. [27], Yan et al. [26], and Chen and Kuo [37]. It was reported that hemicellulose is very reactive and was nearly completely removed at 200 °C, while both cellulose and lignin can be dissolved partially at higher temperatures. Shaw [38] performed steam explosion on poplar and wheat straw at 200–205 °C, steam pressure of 1.66–1.73 MPa for 4–4.5 min. This author reported a decrease in cellulose and hemicellulose content with an increase in the lignin content after the steam explosion treatment of both biomass samples.

Chen and Kuo [33], Yang et al. [39], and Khezami et al. [40] studied the effects of thermal process on biomass. These researchers showed that thermal pretreatment removes moisture and light volatiles from biomass. Bergman et al. [41] and Lipinsky et al. [42] reported that during the torrefaction process, biomass was partly decomposed giving off various condensable and non-condensable gases, with a carbon rich solid as a final product. Mohammad and Karimi [43] reported a corresponding decrease in total sugar recovery with increasing temperature during steam explosion.

3.3. *Ultimate analysis of steam exploded and non-treated barley straw grind*

Table 6 shows that the elemental composition of biomass was dependent on the severity of the treatment condition. Increased carbon content of biomass resulted from higher severity of steam explosion pretreatment. The initial carbon and oxygen content of the non-treated barley straw was 42.30% and 50.99%, respectively. After the steam pretreatment (at 160–180 °C, 8% mass fraction of water, and 5 min retention time), the carbon content increased to a maximum of 46.69–46.89%, while the oxygen content decreased to 45.76–46.77%.

The carbon content of the steam exploded solid product significantly increased ($P < 0.01$) as a function of temperature and retention time, while hydrogen and oxygen content decreased. The carbon content increased from 43.65% to 45.54% as the retention time increased from 5 to 10 min (at 180 °C and 50% mass fraction of water). However this was not the case for all the collected data. Similar results have been obtained from the ultimate analysis performed on thermal pretreated biomass feedstock by Ferro et al. [27] and Yan et al. [26]. Angles et al. [31] reported that the carbon content of the steam exploded pretreated samples increases because lignin condenses and even carbonizes. This condensation may be accompanied by water loss as evidenced by a decrease in oxygen content within the pretreated lignin. Loss in hydrogen and oxygen may be due to the formation of water and carbon monoxide and dioxide.

The reactions that occur during steam explosion generally cause smaller hydrocarbon molecules (volatiles and gases, not recorded in this current study) with low energy density to volatilize or escape, which in turn increase the energy density of the remaining carbon-rich solids. The results obtained from this current elemental ultimate analysis is consistent with the results shown in Tables 3–5, indicating that at higher temperature and retention times, there was carbonization (increase in carbon content), degradation of the sugars (cellulose and hemicellulose), breakdown of the biomass matrix (cross-linking lignin), all of which subsequently led to higher yield of the total soluble lignin moieties during the two step acid hydrolysis. The nitrogen content also increased with increasing process temperature and retention time.

Table 6 – Elemental composition of steam exploded and non-treated barley straw grind.

Temp. (°C)	M.C. (%)	RT (min)	N (%)	C (%)	S (%)	H (%)	O* (%)
NT	8	–	0.31 (0.01)	42.30 (0.04)	0.17 (0.08)	6.23 (0.15)	50.99 (0.08)
140	8	5	0.37 (0.02)	42.49 (0.01)	0.07 (0.01)	6.37 (0.03)	50.70 (0.00)
160	8	5	0.35 (0.02)	46.89 (2.84)	0.05 (0.00)	6.96 (0.44)	45.76 (3.29)
180	8	5	0.41 (0.00)	46.69 (0.04)	0.05 (0.01)	6.08 (0.02)	46.77 (0.06)
140	30	5	0.34 (0.01)	42.17 (0.06)	0.04 (0.01)	6.38 (0.01)	51.07 (0.07)
160	30	5	0.34 (0.01)	42.67 (0.03)	0.09 (0.03)	6.31 (0.03)	50.60 (0.05)
180	30	5	0.38 (0.00)	45.19 (0.04)	0.04 (0.01)	6.11 (0.03)	48.28 (0.08)
140	50	5	0.37 (0.01)	42.10 (0.02)	0.04 (0.01)	6.41 (0.02)	51.07 (0.04)
160	50	5	0.37 (0.00)	43.25 (0.17)	0.26 (0.05)	6.58 (0.05)	49.54 (0.27)
180	50	5	0.39 (0.00)	43.65 (0.03)	0.12 (0.02)	6.30 (0.01)	49.55 (0.05)
140	8	10	0.35 (0.01)	43.04 (0.07)	0.07 (0.01)	6.33 (0.05)	50.21 (0.13)
160	8	10	0.38 (0.01)	42.83 (0.26)	0.08 (0.01)	6.19 (0.09)	50.53 (0.36)
180	8	10	0.43 (0.01)	46.66 (0.07)	0.08 (0.01)	6.15 (0.01)	46.67 (0.07)
140	30	10	0.36 (0.01)	42.39 (0.04)	0.05 (0.01)	6.29 (0.02)	50.91 (0.04)
160	30	10	0.39 (0.01)	41.93 (0.20)	0.12 (0.05)	6.22 (0.03)	51.34 (0.28)
180	30	10	0.44 (0.00)	46.63 (0.21)	0.07 (0.00)	5.91 (0.06)	46.95 (0.28)
140	50	10	0.38 (0.01)	42.01 (0.03)	0.09 (0.00)	6.35 (0.04)	51.17 (0.06)
180	50	10	0.46 (0.01)	45.54 (0.30)	0.07 (0.01)	6.11 (0.05)	47.83 (0.34)

Value in parentheses = standard error; number of replicates, $n = 2$; Temp. = temperature; M.C. = moisture content (% mass fraction); RT = retention time; min = minute; N = Nitrogen; C = Carbon; S = Sulfur; and H = Hydrogen; NT = non-treated; std = standard; O* = oxygen obtained by difference; NT = non-treated biomass; all % values are in mass fraction.

As the moisture content of barley straw grind increased from 8 to 50% (mass fraction of water) at 180 °C and 5 min retention time, the carbon content decreased accordingly from 46.69% to 43.65%, while the hydrogen and oxygen contents increased from 6.08% and 46.77% to 6.30% and 49.55%, respectively. The change in carbon, hydrogen, and oxygen content were consistent and significant, but less dramatic at high moisture content. This implies that higher energy is required to evaporate the moisture before carbonization of the sample starts. The statistical analysis shows that moisture content significantly affected ($P < 0.01$) the carbon content of the steam exploded biomass.

3.4. *Higher heating value of steam exploded and non-treated biomass*

From Table 7, the H/C and O/C ratios were relatively constant with temperature, moisture content, and retention time. There is a close relationship between the theoretical HHV (17.31 MJ kg^{-1}) of barley straw (reported by Annamalai et al. [17].) and the experimentally obtained HHV (17.47 MJ kg^{-1}) of the non-treated barley straw (from this current investigation). The HHV of the solid product increased with temperature and decreased with increasing moisture content. The HHV increased by up to a maximum of about 11% as compared with

Table 7 – Ratio of elemental composition, degree of carbonization, higher heating value, mass yield, and energy recovery of steam exploded pretreated and non-treated barley straw grind.

Tempt. (°C)	M.C. (%)	RT (min)	H/C	O/C	%DOC	HHV (MJ kg^{-1})	MY (%)	ER (%)
NT	8	–	0.15	1.21	–	17.47	–	–
140	8	5	0.15	1.19	1.00	17.51	95.14	95.35
160	8	5	0.15	0.98	1.00	17.52	77.30	77.51
180	8	5	0.13	1.00	1.11	19.36	82.55	91.45
140	30	5	0.15	1.21	1.00	17.46	85.51	85.47
160	30	5	0.15	1.19	1.00	17.46	69.90	69.84
180	30	5	0.14	1.07	1.06	18.61	74.25	79.07
140	50	5	0.15	1.21	1.01	17.57	84.75	85.21
160	50	5	0.15	1.15	1.02	17.75	85.26	86.62
180	50	5	0.14	1.14	1.03	18.05	80.76	83.42
140	8	10	0.15	1.04	1.00	17.48	93.90	93.92
160	8	10	0.14	1.18	1.01	17.67	87.99	89.00
180	8	10	0.13	1.00	1.09	19.00	73.17	79.56
140	30	10	0.15	1.20	1.00	17.52	81.61	81.83
160	30	10	0.15	1.22	1.00	17.52	96.14	96.37
180	30	10	0.15	1.22	1.09	19.02	78.45	85.39
140	50	10	0.15	1.22	1.00	17.48	76.53	76.56
180	50	10	0.13	1.05	1.07	18.64	70.81	75.53

Tempt. = temperature; M.C. = moisture content (% mass fraction); RT = retention time; min = minute; C = Carbon; H = Hydrogen; O = oxygen; DOC = degree of carbonization; HHV = higher heating value; MY = mass yield; ER = energy recovery; NT = non-treated biomass; $n = 2$.

the non-treated biomass. This is a reflection of the increased carbon content with decreased in oxygen content as the temperature increased. ANOVA showed that temperature and moisture content significantly affected ($P < 0.01$ and $P < 0.05$, respectively) the HHV.

Lam et al. [32] and Kumar et al. [44] reported an increase in HHV, lignin, and ash content after steam pretreatment of whitewood samples. Yan et al. [26] reported increased HHV with temperature resulting from thermal pretreatment of loblolly pine. Adapa [30] determined the HHV of the non-treated and steam exploded (at 180 °C, steam pressure of 900 kPa for 4 min) barley straw and found the HHV of non-treated and steam exploded barley straw to be 16.40 MJ kg^{-1} and 17.40 MJ kg^{-1}, respectively. Cellulose, hemicellulose, and lignin are the major components of lignocellulosic biomass. Therefore, any chemical, physical, or structural changes in their composition could potentially lead to changes in the HHV of the biomass.

This investigation shows that reaction temperature is a significant variable in pretreatment processes; increasing temperature caused a reduction in both mass yield and energy recovery. However, this trend was not consistent in all cases. Statistical analysis showed that temperature significantly affected ($P < 0.01$) the mass yield and energy recovery of the steam exploded biomass. This mass loss may be associated with the decomposition/degradation of some reactive components of the hemicellulose (such as acetic acid), as well as moisture loss. At high residence times, the mass loss can be attributed to the decomposition of the less reactive components of the hemicellulose. This two-step nature of the carbonization process (decomposition of reactive and less reactive components of biomass) has been reported by Arias et al. [45], who investigated the influence of carbonization on the grindability and reactivity of woody biomass. Yan et al. [26] reported a similar trend in the thermal pretreatment of loblolly pine, where there was a decrease in the mass and energy yield of the pretreated biomass as the reaction temperature increased. This may be associated to the loss of some volatiles and gases during the thermal pretreatment process. Over the moisture content ranges studied, wet biomass resulted in a lower mass yield and energy recovery as compared to drier biomass with higher mass yield and energy recovery.

3.5. *Degree of carbonization (DOC)*

The DOC increased with temperature and slightly decreased with moisture content of the biomass. This again shows that the water present in the biomass acts as a damper to reduce the severity of the pretreatment conditions. Analysis of variance showed that temperature played a significant role (with $P < 0.01$) on the DOC of the steam exploded biomass. Tooyserkani et al. [29] steam pretreated wood species (10% mass fraction of water) at 220 °C for 5 min to determine the DOC (torrefaction). The authors reported that the calorific value increased as a result of steam explosion with the highest increase of 26% for spruce, from 18.7 MJ kg^{-1} to 23.6 MJ kg^{-1}. It was also reported that there was a significant increase in the ash content. The ash content almost doubled from 2.11% to 4.13% after steam explosion. In this study, we observed the following as indicators of carbonization: color, HHV, carbon content, lignin content, sugars, and ash content.

3.6. *Color analysis*

Table 8 shows the mean values of the color parameters of L^*, a^*, and b^* of the steam exploded and non-treated samples. Color characteristics of the steam explosion pretreated samples are a reflection of the severity of the pretreatment conditions. The lightness (L^*) of steam exploded ground barley

Table 8 – Color characteristics of steam exploded and non-treated ground barley straw.

Temp. (°C)	Moisture content (% mass fraction)	Retention time (min)	L^*	a^*	b^*	ΔE^*
NT	8	–	60.83 (0.01)	7.67 (0.01)	20.36 (0.02)	–
140	8	5	55.82 (0.01)	8.31 (0.01)	16.97 (0.01)	6.08 (0.01)
160	8	5	54.68 (0.00)	9.13 (0.01)	18.24 (0.01)	6.67 (0.02)
180	8	5	29.90 (0.02)	7.23 (0.03)	8.24 (0.02)	33.22 (0.02)
140	30	5	57.10 (0.01)	8.74 (0.00)	20.29 (0.02)	3.88 (0.01)
160	30	5	47.60 (0.00)	9.03 (0.01)	20.11 (0.01)	13.30 (0.01)
180	30	5	32.93 (0.02)	9.08 (0.00)	13.35 (0.02)	28.80 (0.00)
140	50	5	50.37 (0.00)	9.01 (0.00)	19.16 (0.01)	10.61 (0.01)
160	50	5	41.78 (0.00)	8.28 (0.01)	15.65 (0.01)	19.63 (0.01)
180	50	5	31.59 (0.01)	6.75 (0.01)	7.40 (0.02)	32.00 (0.02)
140	8	10	53.15 (0.01)	9.20 (0.00)	19.34 (0.00)	7.89 (0.01)
160	8	10	45.90 (0.01)	10.18 (0.01)	17.24 (0.01)	15.46 (0.01)
180	8	10	30.98 (0.00)	9.18 (0.01)	12.45 (0.02)	30.91 (0.01)
140	30	10	51.07 (0.00)	9.23 (0.01)	17.68 (0.01)	10.24 (0.01)
160	30	10	50.99 (0.01)	9.58 (0.00)	19.16 (0.01)	10.09 (0.01)
180	30	10	30.44 (0.01)	8.01 (0.01)	8.53 (0.01)	32.62 (0.01)
140	50	10	47.65 (0.01)	9.25 (0.00)	17.94 (0.00)	13.49 (0.01)
180	50	10	30.41 (0.01)	6.58 (0.01)	7.14 (0.00)	33.18 (0.01)

Value in parentheses = standard error; number of replicates, $n = 3$; Temp. = temperature; The scale L^* represents from 0 for black to +100 for white; The a^* and b^* have no specific numerical limits; Positive a^* is red; Negative a^* is green; Positive b^* is yellow; Negative b^* is blue; and ΔE^* = total color difference.

straw decreased by up to a maximum of about 51% with increasing temperature and retention time. This implies that, the higher was the severity of the pretreatment conditions, the darker were the pretreated samples. In most cases, the yellowness of the steam exploded samples decreased with increasing temperature and retention time, except for samples pretreated at 160 °C, moisture content of 8–30% (mass fraction of water) and at 5–10 min retention time. Increasing blueness also signifies that the samples got darker as the severity of pretreatment increased with respect to increasing temperature and retention time.

The lightness (L^*) and yellowness (b^*) of the non-treated ground barley straw were higher as compared to the steam pretreated samples as it is evident in Fig. 4a. The calculated differential color composite ΔE^* is a good indicator of color deviation between pretreated and non-treated samples. The total color difference between the steam exploded and non-treated samples increased with increasing temperature and retention time. The highest total color difference was observed at 180 °C. Further studies may be required to rapidly estimate and correlate color and HHV of steam exploded biomass at various severity factors. The color of steam pretreated samples can be used as an indicator of carbonization during steam explosion pretreatment, as samples tended to darken with increased carbonization [29]. Zhang and Cai [46] reported that the color changes observed in wood during steam treatment were a result of a series of chemical reactions. These are primarily due to the reactions between the chemical constituents of wood cell wall and extractives under high temperature and humidity conditions. Cellulose and hemicellulose are polysaccharides that can cause significant changes at a critical temperature of 120 °C. Cellulose degrades to yellow when the temperature is above 140 °C [46]. From the collected data in this study, hemicellulose was more sensitive to temperature and easier to degrade than cellulose. During steam explosion pretreatment, furfural and some polysaccharides with low molecular weights were generated from the degradation of hemicellulose [46]. Changes in lignin and extractives can also contribute to the color changes. Carboxylates and phenol may be produced within the lignin or extractive molecules at high temperatures and humidity [46]. All these put together may lead to the current color changes in the ground barley straw during steam explosion pretreatment.

4. Conclusions

The operating reaction temperature, retention time, and moisture content of biomass barley straw grind were studied to investigate the dynamics responsible for the changes in the steam exploded barley straw. The severity factor, chemical compositions, ultimate elements, higher heating value, and color characterization of pretreated barley straw were used as indicators to evaluate the effects of the main factors. The results obtained from this investigation provided qualitative and quantitative insights into the responses of hemicellulose, cellulose, and lignin in barley straw to the steam explosion process at various levels of the variables tested. Higher temperature and retention time resulted to the breakdown of the lignified barley straw matrix with increase in the total acid soluble lignin by up to a maximum of about 33%. The AIL increased with increasing temperature and decreasing moisture content by up to a maximum of about 91.28% as compared to the non-treated biomass. Both HHV and carbon content increased by up to a maximum of about 11%, while the severity factor increased correspondingly with increasing temperature and retention time. The lightness (L) of steam exploded ground barley straw decreased by up to a maximum of about 51% with increasing temperature and retention time. Therefore, it is clear that the thermal degradation of cellulose and hemicellulose in barley straw are different from each other due to the crystalline nature of the former and the amorphous nature of the latter compound. The high initial moisture content of ground barley straw has buffer effect by lessening the effect of harsher pretreatment conditions. Based on the collected data, barley straw can be used as a potential feedstock for the biofuel industry.

Acknowledgments

The authors acknowledge the financial support of the Natural Sciences and Engineering Research Council of Canada and Agriculture and Agri-Food Canada through the Agricultural Bioproduct Innovation Program. Acknowledgment goes to Dr. Thomas Canam and Ms. Jennifer Town at Agriculture and Agri-Food Canada for their technical assistance. The support from Zahra Tooyserkani and Bahman Ghiasi of the Department of Chemical and Biological Engineering, University of British Columbia and the technical support unit (Blondin Richard and Bill Crerar) of Chemical and Biological Engineering Department, University of Saskatchewan is highly appreciated.

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